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First-principles study of magnetic interactions in cupric oxide

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Cupric oxide (CuO) has been described as belonging to the quasi-one-dimensional antiferromagnetic compounds. It has also been suggested that cupric oxide possesses strong magnetic anisotropy, which is possibly related to the observed ferroelectricity in this material. In this paper, the magnetic interactions of CuO are investigated using the embedded cluster approach. Accurate wave-function-based methods have been employed to describe the interactions along all copper-oxygen chain directions. Both two-center and three-center clusters are considered in our calculations. The antisymmetric anisotropic interaction parameters are also calculated for the two-center clusters by applying an effective Hamiltonian theory. Our results show that the magnetic interactions are dominated by the antiferromagnetic coupling between copper ions along the chain of largest Cu-O-Cu angles in agreement with experiment. The results for the interplane magnetic interactions reveal competition between nearest-neighbor ferromagnetic coupling and second-nearest-neighbor antiferromagnetic interaction along the direction where two copper ions are connected via doubly bridged oxygen ligands. We also find nonnegligible Dzyaloshinskii-Moriya interactions with magnitude comparable to the weak isotropic interchain interactions.

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I. INTRODUCTION

Among the cuprate compounds, cupric oxide (CuO) has the simplest chemical composition. Nevertheless, CuO is closely related to high-T_c superconducting cuprate compounds in many aspects, including structural and magnetic properties. The main motivation for early studies on CuO was that part of the physics of high-T_c superconductors can be explained by studying this compound. Cupric oxide itself exhibits unusual magnetic properties,[1–5] which deserve detailed study. Furthermore, it was observed more recently that in cupric oxide a magnetoelectric coupling occurs at its incommensurate antiferromagnetic phase, which exists in a temperature range of 212–230 K.[2,3,5] This suggests that CuO is an interesting candidate in the search for high-temperature magnetoelectric multiferroics.[6]

The crystal structure of CuO has been reported by many authors (see for example Refs. 3,4,6–8) to have the monoclinic $C2/c$ space group. This structure is rather unique among the transition-metal oxides which mostly have a cubic rocksalt or perovskite-type structure. It has been shown that rather than a distorted CuO_6 octahedron, the Cu-O coordination in cupric oxide is more properly described as a plane of CuO_4 coordination (see Fig. 1).[7] An inversion center is located in each of the copper ions, and a C_2 axis is centered at the oxygen ions. The chemical unit cell contains four Cu atoms and four oxygen atoms.

The investigation of magnetic properties of cupric oxide has a long history. A phase transition between a paramagnetic and an antiferromagnetic phase was observed to occur at a Néel temperature of about 230 K, for instance by a magnetic susceptibility[1] measurement and by several hyperfine interaction studies.[9] These results were then refined by other magnetic susceptibility,[4,10,11] specific heat,[10] neutron diffraction,[2,5] and neutron scattering[3] studies which showed that CuO undergoes successive magnetic transitions at $T_{N1} = 230$ K and $T_{N2} = 212$ K without any important structural phase transitions. Below T_{N2}, the structure is collinear antiferromagnetic with a propagation vector of $(\frac{1}{2}\ 0\ \bar{\frac{1}{2}})$ (see Fig. 1).[2,3,5] Between T_{N1} and T_{N2}, the magnetic structure is incommensurate with different propagation vectors reported by different authors, as summarized by Aïn *et al.*[5] Nevertheless, all authors report only small incommensurability in this phase; e.g., Forsyth *et al.* observed a propagation vector of $(0.506\ 0\ -0.483)$.[2] The magnetic susceptibility measurement reported by O'Keeffe *et al.*[1] and then confirmed more recently by Köbler *et al.*[11] displayed a broad maximum in the susceptibility curve at $T_{\max} = 540$ K, much higher than the Néel temperatures. This suggests a low dimensionality of the magnetic structure. A comparison between 1D and 2D Heisenberg models to predict the relation between J and $T_{\max}$ revealed that a quasi-1D model is a better approximation for this compound.[12] In the ac planes, antiferromagnetic ordering has been found.[2] The magnetic interaction J has been determined to be 91 meV from magnetic susceptibility measurements[1] and 67 ± 20 meV by fitting inelastic neutron scattering data,[3] assuming a quasi-one-dimensional model.

There are several theoretical studies concerning magnetic interactions in cupric oxides appearing in the literature. The first study is the spin dimer analysis of Koo *et al.*[13] which employed the extended Hückel method. Later several DFT-based periodic band structure calculations[14–16] appeared. All these results reproduced well the experimental results of Yang *et al.*,[3] Arbuzova *et al.*,[4] and Aïn *et al.*[5] that the strongest interaction is antiferromagnetic and along the $[10\bar{1}]$ direction. In addition, the periodic calculations indicated that the magnetic structure of CuO favors a configuration in which the copper ions are coupled antiferromagnetically along the $[10\bar{1}]$ chain and ferromagnetically in the [101] chain. In periodic calculations, the energies of different spin configurations are mapped using classical energy expressions to obtain the

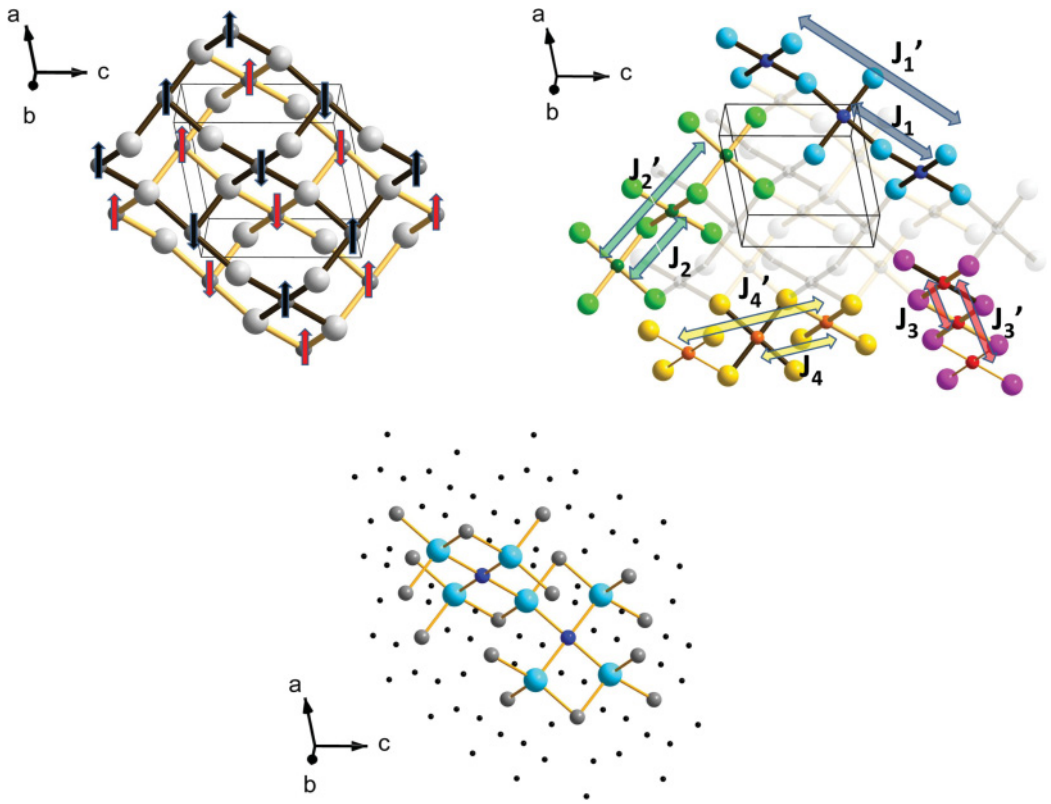

FIG. 1. (Color online) Top left: The unit cell of CuO and the two neighboring Cu-O layers in the *ac* planes, displayed using different light and dark brown bonds. The light and dark gray balls represent oxygen and copper atoms, respectively. The spins are ordered antiferromagnetically along the $[10\bar{1}]$ chain and ferromagnetically along [101]. Top right: The clusters used in this work are displayed with the blue, green, red, and gold balls to represent clusters 1, 2, 3, and 4, respectively. Clusters 1 (blue) and 2 (green) are denoted in-plane clusters, while clusters 3 (red) and 4 (gold) are denoted interplane clusters. Bottom: The embedding scheme used to describe cluster 1 with two-copper centers, as explained in Sec. II. The cluster consists of two copper ions (dark blue balls) and seven oxygen ligands (light blue balls, thus a Cu_2O_7 cluster). The nearest copper ions (gray balls) are described using model potentials, and finally the electrostatic potential from the rest of the crystal is modeled using optimized point charges. Other clusters are built in a similar way.

coupling constants. One of the objectives of the current study is to perform explicit quantum mechanical calculations to discuss the different magnetic interaction parameters, both isotropic and anisotropic. The term *anisotropic interactions* used here refers to the *anisotropic exchanges* caused by spin-orbit coupling which differentiates the magnetic anisotropy axes, and should not be confused with the *different values of isotropic interactions J* along different crystallographic axes.

The more general discussion on the nature of magnetic anisotropy in cuprates has been reported in many works decades ago (see for example Refs 17–19). By taking into account the spin-orbit interaction in describing the mechanisms of magnetic interactions, it has been shown that the antisymmetric interaction can become the largest anisotropic correction to the superexchange when the crystal symmetry is sufficiently low.[17] In addition, Moriya explained that the direction of this antisymmetric interaction, which is also called the Dzyaloshinskii-Moriya (DM) interaction, between two magnetic ions is determined by the symmetry relating these ions—the so-called Moriya rules. Thus in general the DM interaction depends on the crystal symmetry. In this paper, our analysis of the calculated DM interactions for the considered clusters will be based on these symmetry considerations.

We present quantum chemical calculations to study the magnetic interactions in CuO and to extract magnetic anisotropic interaction parameters[20–22] in a real cuprate material, using an embedded cluster approach, the details of which will be explained in Sec. II. In order to check the validity of the cluster model, we compare the parameters obtained from a periodic band structure calculation with those obtained by using the cluster descriptions at the same level of theory. Once the clusters are validated, the results of more accurate calculations will be discussed. The isotropic interactions between the nearest-neighbor and second-nearest-neighbor copper ions are calculated using the accurate difference-dedicated configuration interaction method.[23] Furthermore, the nearest-neighbor intersite antisymmetric anisotropy parameters in CuO which, to the best of our knowledge, are not available from the literature are also extracted. By knowing the amplitudes of these interactions, one may estimate the most important mechanisms giving rise to the magnetic anisotropy in this compound.

This paper is organized as follows: The computational setup for the calculations is explained briefly in Sec. II. The next section presents the theoretical framework used in this work. Section IV reports and discusses the results of the calculations. The conclusions will be presented in the final section.

II. COMPUTATIONAL INFORMATION

We discuss the different magnetic interactions in cupric oxide (CuO) using the so-called embedded cluster approach. This approach is well suited for the description of local electronic structure properties of extended solid state materials, provided that the clusters used in the calculations are well chosen. Using the embedded cluster description, one is then able to treat the electron correlation using an accurate wave-function-based method. Many articles have been published in which the magnetic coupling in ionic insulators has been successfully calculated (see for example Refs. 24–27). Furthermore, access to the wave functions enables one to extract parameters using effective-Hamiltonian theory.[28] The application of this theory to magnetic solids has provided information about, among others, the magnetic coupling and the hopping integral, thus rationalizing the *t-J* model,[29] the cyclic four-spin operator,[30] and the two- and three-body biquadratic exchange.[31] In the present study, we apply the effective-Hamiltonian approach to obtain the isotropic and anisotropic magnetic interaction parameters in the material of interest, CuO.

The magnetic ordering has been determined to be in the *ac* planes,[2] implying that CuO can be viewed as being composed of two Cu-O chains running along the [101] and [10$\bar{1}$] directions, forming a plane (see Fig. 1). The geometry used in this work is the one at room temperature reported by Yamada *et al.*[8] The Cu-O distances are 1.95 Å and 1.96 Å along the [101] and [10$\bar{1}$] chains, respectively. These distances are almost identical. But since the Cu-O-Cu angles are different (approximately 109° along the [101] chain compared to 146° along the [10$\bar{1}$] chain), the Cu-Cu distances differ quite largely, 3.17 Å along [101] and 3.75 Å along [10$\bar{1}$]. We performed *ab initio* calculations for embedded clusters containing two- and three-copper centers along these directions (clusters 1 and 2; see Fig. 1). In addition to the in-plane cluster calculations, we have also performed calculations to two- and three-copper centers involving ions on different layers to study the interlayer interactions. Two copper ions located at neighboring layers are connected in two ways: by edge-sharing and by corner-sharing CuO_4 units (clusters 3 and 4, respectively; see Fig. 1). We consider all four different cases in our calculations. In the following discussions, two- and three-center clusters refer to clusters involving these two- and three-copper ions, respectively.

The copper ions, together with the bridging and the nearest neighboring oxygen ligands, form the cluster, which is embedded in a number of point charges to mimic the Madelung potential of the crystal environment. The nearest neighboring copper ions to the cluster are described by model potentials to give a better representation of their charge distribution and to avoid excessive polarization of the cluster toward the positively charged environment (see Fig. 1). In order to see the dependence of the calculated magnetic coupling parameters to the temperature, the same calculations have been carried out for different geometrical structures reported by Yamada *et al.*[8] for various temperatures ranging from 150 to 300 K, but no significant differences on the results were observed.

We have performed complete active space SCF (CASSCF) calculations with the minimal active space having only the magnetic orbitals in the active space. This level of calculation only involves minimal electron correlation in the wave function, almost equal to that of an open-shell Hartree-Fock calculation. Therefore, in addition to these calculations, dynamic electron correlations are taken into account by employing the difference-dedicated configuration interaction (DDCI) method.[23] The DDCI wave function consists of determinants which are obtained from the minimal CAS and all the single and double excitations, except the double excitations from the inactive space to the virtual space. Since these doubly excited determinants from the inactive to virtual spaces only shift the diagonal matrix elements, only the total energy of a particular state will be affected by the removal of these determinants, but the energy difference between two states will hardly be changed.[23] Therefore this DDCI method is specially designed to calculate energy differences, and has been proven to be able to describe accurately the magnetic couplings in transition-metal compounds (see for example Ref. 32). The inclusion of spin-orbit coupling in our calculation is accomplished via a spin-orbit configuration interaction of the CASSCF solutions, using the spin-orbit restricted active space state interaction (SO-RASSI) method.

The CASSCF and SO-RASSI calculations are performed with the MOLCAS 7.4 code,[33,34] while for the DDCI calculations, we use the CASDI[35,36] code. In all calculations, the copper and oxygen ions in the clusters have been described by using the ANO-RCC basis sets[37] implemented in MOLCAS 7.4, and we use the following contraction schemes: $(6s5p4d2f)$ for Cu and $(4s3p1d)$ for O. However, previous studies showed that the incorporation of f basis functions tends to slightly underestimate the magnetic coupling constants obtained with DDCI.[38] Therefore, for our DDCI calculations, we exclude the f basis functions of Cu. In order to test our cluster model, we perform periodic spin unrestricted Hartree-Fock calculations implemented in the CRYSTAL09 program package[39,40] using smaller 6-31G basis sets.[41–43]

III. THEORETICAL FRAMEWORK

The isotropic and anisotropic magnetic interaction parameters in the two-center clusters described in the previous section are extracted by using a recently proposed scheme which has been successfully applied to monometallic[20] and bimetallic complexes.[21] This scheme uses the information contained in the matrix elements of an effective-Hamiltonian interaction matrix which is obtained by applying effective-Hamiltonian theory.[28] The effective-Hamiltonian is compared with the model Hamiltonian used in phenomenological studies. For our two-center clusters, we use the following formulation for the phenomenological Hamiltonian:

$$\hat{\mathcal{H}}_{\text{two}} = J\hat{S}_1 \cdot \hat{S}_2 + \vec{d}\hat{S}_1 \times \hat{S}_2 + \hat{S}_1 \cdot \mathbf{D} \cdot \hat{S}_2, \qquad (1)$$

where J is the isotropic magnetic interaction parameter between two nearest-neighbor copper ions, $\vec{d}$ is the DM vector, and $\mathbf{D}$ is a second-rank symmetric anisotropic tensor. In the basis of $|S, M_S\rangle$, the Hamiltonian in Eq. (1) transforms to

TABLE I. Norm of the DM vector (in meV) calculated for cluster 1 at different levels of theory.

	CAS(2,2)SCF	CAS(2,2)PT2	CAS(18,10)SCF	CAS(18,10)PT2
$\lvert\vec{d}\rvert$	1.41	1.41	1.38	1.41

the following model Hamiltonian matrix in the magnetic axes frame (defined with the symmetric anisotropy tensor):

$$\begin{array}{lcccc} \hat{H}_{\text{two}} & |1,-1\rangle & |1,0\rangle & |1,1\rangle & |0,0\rangle \\ \langle 1,-1| & \frac{1}{4}J+\alpha & 0 & \delta & \frac{\sqrt{2}}{4}(d_y+id_x) \\ \langle 1,0| & 0 & \frac{1}{4}J+\beta & 0 & -\frac{i}{2}d_z \\ \langle 1,1| & \delta & 0 & \frac{1}{4}J+\alpha & \frac{\sqrt{2}}{4}(d_y-id_x) \\ \langle 0,0| & \frac{\sqrt{2}}{4}(d_y-id_x) & \frac{i}{2}d_z & \frac{\sqrt{2}}{4}(d_y+id_x) & -\frac{3}{4}J+\gamma \end{array} \tag{2}$$

where α, β, and γ are spin-orbit corrections to the isotropic coupling constant coming from the axial symmetric anisotropy, and $\gamma = -2\alpha - \beta = 0$ since we assume a traceless anisotropic tensor **D**. δ accounts for the rhombic symmetric anisotropy.

In a recent study,[44] Maurice *et al.* showed for related compounds that the symmetric contribution to the anisotropic interaction is very small and computationally demanding compared to the antisymmetric contribution. Therefore, for the present study, we decide to focus only on the isotropic and antisymmetric anisotropic terms. Hence we only discuss the first two terms of the Hamiltonian in Eq. (1).

Another recent study has shown that in contrast to the isotropic interaction, the norm and direction of the DM vector are nearly unaffected by the extension of the size of the active space or by the second-order perturbation corrections to the corresponding reference wave functions.[22] This indicates that the main contributions to the DM interaction are from the direct spin-orbit coupling between the lowest lying singlet and triplet states. We have also tested the dependence of the calculated norms of $|\vec{d}|$ to various levels of calculation. See Table I for the calculations on cluster 1. The CAS(2,2) involves only the magnetic electrons and orbitals, while the CAS(18,10) has all electrons in the *d* orbitals in the active space and the state interaction space consists of 25 singlet and 25 triplet states. The calculated values are almost unchanged. Thus the extraction of the antisymmetric interaction will only be discussed at the minimal CASSCF level. The strategy to extract the parameters is described in detail in the previous report.[22]

In order to get access to the next-nearest-neighbor magnetic interactions, three-center clusters are needed. Here, a somewhat simpler scheme has been employed, extracting only the isotropic interaction parameters. This leads to the following formulation for the Hamiltonian:

$$\hat{\mathcal{H}}_{\text{three}} = J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3) + J'\hat{S}_1 \cdot \hat{S}_3, \tag{3}$$

where J' is the next-neighbor isotropic interaction between $\hat{S}_1$ and $\hat{S}_3$. These coupling constants are directly related to energy differences, and since the ions are described as spin-only systems ($S = \frac{1}{2}$), the parameters can be extracted by taking the difference of the energy eigenvalues of the low-lying quartet and two doublet states. Thus $J = \frac{2}{3}(E_Q - E_{D_u})$ and $J' = J + (E_{D_u} - E_{D_g})$. Using this convention, $J > 0$ and $J < 0$ indicate antiferromagnetic and ferromagnetic interactions, respectively.

Different sizes of the two-center clusters have been taken. For the corner-sharing nearest-neighbor interactions, J_1, J_2, and J_4, we take Cu_2O_7 clusters (clusters 1, 2, and 4), and the edge-sharing interplane interaction J_3 is described by the Cu_2O_6 cluster (cluster 3; see Fig. 1). Similar choices for the three-center clusters lead to Cu_3O_{10} for clusters 1, 2, and 4, and Cu_3O_8 for cluster 3.

IV. RESULTS AND DISCUSSION

In the first place, it is desirable to check whether the clusters are relevant models to obtain information about the electronic structure of CuO. For that purpose, we have performed a series of unrestricted Hartree-Fock (UHF) broken-symmetry periodic calculations to different spin configurations. The magnetic coupling parameters are extracted using an Ising model Hamiltonian with only nearest-neighbor interactions, $H_{\text{Ising}} = \Sigma_{\langle ij\rangle} J_{ij}^{\text{Ising}} S_i^z S_j^z$. The obtained values are compared to the magnetic coupling parameters which are obtained from UHF calculations of the two-center clusters by using an Ising model Hamiltonian $H_{\text{Ising}} = J^{\text{Ising}} S_1^z S_2^z$. It must be noted that in this comparison we do not attempt to obtain very accurate numbers, but rather we only check whether there is an important artificial effect due to the size of the chosen clusters and the way to embed them. The results are shown in Table II. As can be seen, the agreement between the cluster and periodic approaches provides the validity of our cluster description. Moreover, our periodic UHF calculations also indicate that the magnetic ground state has parallel spins along the [101] direction and antiparallel spins in the $[10\bar{1}]$ direction, in agreement with the previous periodic DFT calculations.[14–16] However, Table II also shows that the in-plane and interplane interactions appear at equal strength, suggesting that CuO does not really belong to the one-dimensional antiferromagnetic compounds, which disagrees with experimental findings.[1,11] We shall see that this is due to the use of a spin-unrestricted approach at the Hartree-Fock level. Semiempirical approaches to the DFT calculations,

TABLE II. The calculated magnetic coupling constants (in meV) from the calculations of two-center cluster models and a periodic approach at the UHF level.

	Cluster	Periodic
J_1^{Ising}	10.4	12.8
J_2^{Ising}	−2.9	−4.3
J_3^{Ising}	−7.5	−7.7
J_4^{Ising}	−3.4	−3.7

TABLE III. The calculated magnetic interactions at DDCI level (in meV).

Two-Center		Three-Center		
Cluster	J	J	J'	Cluster
1 (Cu_2O_7)	47.4	47.5	0.1	1 (Cu_3O_{10})
2 (Cu_2O_7)	1.4	0.8	−0.0	2 (Cu_3O_{10})
3 (Cu_2O_6)	−9.9	−9.0	5.1	3 (Cu_3O_8)
4 (Cu_2O_7)	−3.4	−3.7	0.0	4 (Cu_3O_{10})

either by introducing an effective internal energy U to the LDA Hamiltonian or mixing LDA and exact Hartree-Fock exchange functionals, can recover coupling constants which are in a good agreement with experiment.[15,16] As a better alternative, a Heisenberg Hamiltonian can be treated explicitly to describe the isotropic interactions. In a periodic calculation, however, the use of a Heisenberg Hamiltonian is not easy, since the wave function cannot be made an eigenfunction of S^2. An embedded cluster approach does not suffer from this problem.

Now that the clusters have been validated, we will continue by discussing the results of more accurate calculations using the embedded cluster approach. The nearest-neighbor and next-nearest-neighbor isotropic couplings are obtained using the Heisenberg Hamiltonian. The calculated J values using the DDCI energies are listed in Table III. The data presented in the table are obtained from the spin-orbit-free calculations by taking the energy differences between magnetic states. For the three-center clusters, this means that the coupling constants are obtained from the energy differences between the quartet and the two doublet states, as mentioned in Sec. II, while in the two-center clusters, $J = (E_{\text{triplet}} - E_{\text{singlet}})$. When the spin-orbit coupling is taken into account, the calculated J values turn out to be practically identical to these values because α and β in Eq. (2) are very small and the orbitals are not relaxed in the spin-orbit-coupled wave functions. This implies that spin-orbit coupling hardly affects the isotropic couplings. Furthermore, the values of the nearest-neighbor isotropic coupling constant J from the two-center cluster calculation agree excellently with the same parameters obtained from the corresponding three-center cluster. The transferability from the two-center to the three-center cluster (see Table III) again suggests that our cluster approach has modeled the magnetic properties of the crystal properly.

As already expected from the dependence of the superexchange interaction on the Cu-O-Cu bond angle,[12] the magnetic interaction along the $[10\bar{1}]$ chain is by far the strongest among all. Along this chain (cluster 1), the Cu-O-Cu bond angle is around 146°. The interaction is antiferromagnetic with a coupling constant of 11 meV using the CASSCF wave function to the two-center cluster (not shown in the table) which is still less than 20% of the value of 67 ± 20 meV obtained experimentally by Yang *et al.*[3] The computed value is greatly improved when the DDCI energies are used, and the resulting antiferromagnetic J_1 value of 47 meV is in reasonable agreement with experiment. The slight discrepancy from the experimental value is probably in part due to the fact that the experimental J was roughly estimated by considering only one single J value to obtain the spin-wave velocity $v = Ja$,[3] where a is the Cu-Cu distance along the $[10\bar{1}]$ direction. For a quasi-one-dimensional antiferromagnet, it is common to consider only one J value along the direction where long-range magnetic order is detected to fit the experimental data. However, it should be noted that the J value along this direction, i.e., along $[10\bar{1}]$ in the case of CuO, can be smaller due to the appearance of interchain interactions, even though these are weak. Along the [101] direction (cluster 2) with a Cu-O-Cu bond angle of about 109°, the interaction is very weak and the incorporation of dynamic correlation to the CASSCF wave function changes the interaction from weakly ferromagnetic with a J value of −1 meV to weakly antiferromagnetic with a coupling constant of 1 meV.

Neighboring layers (cluster 3 and 4) are coupled ferromagnetically, and the inclusion of dynamic electron correlation to the minimal CASSCF wave function changes the coupling constant from −3 meV to −10 meV for J_3 and from −1 meV to −3 meV for J_4. The fact that the nearest-neighbor interlayer interaction is ferromagnetic is again due to the small Cu-O-Cu angle,[12] which is about 96° and 104° in clusters 3 and 4, respectively. Nevertheless, these interplane interactions are still much weaker than the in-plane magnetic interaction J_1, by a factor of more than 4. These results support the conclusion that cupric oxide belongs to the quasi-1D-antiferromagnets.

We also observed another interesting feature from the next-nearest-neighbor coupling constant J' calculated by using the three-center clusters. These interactions are small compared to the nearest-neighbor coupling constant J. However, a closer look at cluster 3 shows that J_3' is antiferromagnetic and relatively strong compared to J_3, with a ratio $|\frac{J_3'}{J_3}|$ of more than $\frac{1}{2}$. If one assumes a classical spin-$\frac{1}{2}$ chain with a spin Hamiltonian $\hat{\mathcal{H}}_{\text{classic}} = \Sigma_i \{J_{nn} S_i^z S_{i+1}^z \cos\theta + J_{nnn} S_i^z S_{i+2}^z \cos 2\theta\}$, where θ is angle between the neighboring spins, then a spiral structure with $\cos\theta = -\frac{J_{nn}}{4J_{nnn}}$ can be stabilized as soon as $|J_{nnn}| > \frac{1}{4}|J_{nn}|$. Thus, the strong antiferromagnetic next-nearest-neighbor interlayer interaction along the [111] direction (cluster 3) can be expected to introduce frustration to the ferromagnetic interlayer interaction.

In all calculations mentioned above, the strength of the isotropic coupling at the CASSCF level is enhanced when the dynamic electron correlation is taken into account. Nevertheless, in the calculations on the three-center clusters, due to the large distance of second-nearest copper ions, the incorporation of dynamic electron correlation does not change the interactions significantly.

We continue now to the discussion of the antisymmetric interactions. The vector components and the norms of the calculated DM interactions are displayed in Table IV. In all calculations performed in this work, the clusters have been oriented such that the copper ions and the bridging oxygen ligands lie in the xy plane, and if there is a local C_2 symmetry, the C_2 axis is oriented along the y axis. The mechanisms contributing to the DM vector in two CuO_4 planar coordinations have been analyzed in detail by Maurice *et al.*[22] by a systematic study of copper oxide model systems. Here we will only mention briefly the qualitative picture of these mechanisms. The strongest DM interaction is obtained for a Cu-O-Cu bending angle of about 140°.[22] The dominant

TABLE IV. The components and the norms of the DM vector (in meV), extracted at the CASSCF level using two-center clusters.

Cluster	d_x	d_y	d_z	$\lvert\vec{d}\rvert$
1	−0.26	0.00	−1.39	1.41
2	−0.08	0.00	0.41	0.42
3	0.00	0.00	0.00	0.00
4	0.00	0.00	−0.04	0.04

contribution to the DM interaction is due to the interactions of atomic 3*d* orbitals on the two copper sites. The strongest interaction is therefore obtained when this *d*-*d* interaction is large. This happens when the Cu-O-Cu bending angle is close to 145°, where the contribution of $d_{x^2-y^2}$ and d_{xy} orbitals becomes maximal. The slight deviation from 145° occurs because other mechanisms contribute, such as oxygen-oxygen (*p*-*p*) contributions and oxygen-copper (*p*-*d*) contributions. The latter contribution becomes important when the Cu-O-Cu angle is close to 90°, where the *d*-*d* contributions are significantly reduced due to symmetry. In addition to the Cu-O-Cu bending angle, the twisting of the CuO_4 planes plays also an important role in the mechanism of the DM interaction. When the twist angle is zero, there is a local C_{2v} symmetry, such that the orbitals are only coupled via the $\hat{l}_z \cdot \hat{s}_z$ operator. Then a proper orientation of the clusters only allows $d_{x^2-y^2}$ and d_{xy} orbitals to contribute to the *d*-*d* mechanism. As soon as the two planes are twisted, the lower symmetry allows the other *d* orbitals to contribute.

In cupric oxide, along the $[10\bar{1}]$ direction the Cu-O-Cu bending angle of 146° is expected to enable the optimal contribution of both $d_{x^2-y^2}$ and d_{z^2} orbitals to the *d*-*d* interactions. Beside that, the corner-sharing CuO_4 planes along $[10\bar{1}]$ are twisted with an angle of 78°, which allows the coupling between all 3*d* atomic orbitals. Along all other directions, the Cu-O-Cu bending angle is close to 90°, which reduces the *d*-*d* contribution. Due to the structural connections of the CuO_4 planes in CuO, the strongest antisymmetric interaction is expected to take place in the $[10\bar{1}]$ direction, which is confirmed quantitatively by the norms presented in Table IV. We have also extracted the individual vector components of the antisymmetric interactions (Table IV). Due to the C_2 local symmetries in CuO, the DM vectors of these clusters align on the *ac* plane,[17] since the C_2 axis is actually parallel to the *b* axis. On the cluster 3, $|\vec{d}| = 0$ due to the local inversion symmetry, while on the cluster 4, $|\vec{d}|$ turns out to be practically 0 due to the small Cu-O-Cu bending angle in this direction. The norm of the DM interactions along the $[10\bar{1}]$ direction turn out to be comparable to the interchain isotropic interactions. Therefore, although the antisymmetric interactions are weak, they are nonnegligible.

V. CONCLUSIONS

We have presented in this paper a series of quantum chemical calculations of the magnetic interactions in cupric oxide using wave-function-based methods. Our approach relies on the information contained in the matrix elements of the effective matrix Hamiltonian. The matrix elements are obtained from the *ab initio* wave functions and energies. The results support the conclusion that CuO belongs to the quasi-one-dimensional antiferromagnetic compounds. The use of spin-unrestricted approach may lead to the disappearance of this one-dimensional character. The presence of the incommensurate phase is a signature of competing isotropic interactions or DM interactions, or both. Here we have demonstrated that both exist in CuO. It is interesting to note that even without the presence of spin-orbit coupling, the incommensurate state can also be stabilized by the competition between interplane isotropic interactions. The quantitative agreement of the calculated *J* values with available experimental observations suggests the reliability of our approach.

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